HYDROLOGICAL PROCESSES
Hydrol. Process. **15**, 1251–1269 (2001)
DOI: 10.1002/hyp.212

The behaviour of 39 pesticides in surface waters as a function of scale

Paul D. Capel,[1]* Steven J. Larson[1] and Thomas A. Winterstein[2]

[1] *US Geological Survey, University of Minnesota, Minneapolis, MN 55455, USA*
[2] *US Geological Survey, Mounds View, MN 55112, USA*

Abstract:

A portion of applied pesticides runs off agricultural fields and is transported through surface waters. In this study, the behaviour of 39 pesticides is examined as a function of scale across 14 orders of magnitude from the field to the ocean. Data on pesticide loads in streams from two US Geological Survey programs were combined with literature data from field and watershed studies. The annual load as percent of use (LAPU) was quantified for each of the fields and watersheds and was used as the normalization factor across watersheds and compounds. The in-stream losses of each pesticide were estimated for a model stream with a 15 day travel time (similar in characteristics to the upper Mississippi River). These estimated in-stream losses agreed well with the observed changes in apparent LAPU values as a function of watershed area. In general, herbicides applied to the soil surface had the greatest LAPU values and minimal in-stream losses. Soil-incorporated herbicides had smaller LAPU values and substantial in-stream losses. Insecticides generally had LAPU values similar to the incorporated herbicides, but had more variation in their in-stream losses. On the basis of the LAPU values of the 39 pesticides as a function of watershed area, a generalized conceptual model of the movement of pesticides from the field to the ocean is suggested. The importance of considering both field runoff and in-stream losses is discussed in relation to interpreting monitoring data and making regulatory decisions.

KEY WORDS pesticides; insecticides; herbicides; runoff; stream; load; modelling; surface water

INTRODUCTION

The movement of pesticides from agricultural fields and through the surface water network has been studied extensively. Although each pesticide behaves differently, the processes that govern their behaviour and fate have been identified and, to some extent, quantified. Atrazine was used as an example of a pesticide that exhibits ideal behaviour in its movement from agricultural fields to the ocean (Capel and Larson, 2000). From a field runoff perspective, atrazine is ideal because it is widely used, typically applied on the bare soil surface, and is observed in most runoff events. From a surface water perspective, it is one of the most commonly observed herbicides in streams and rivers, and has relatively slow loss processes from the water column. By using the parameter of annual load (in field runoff or in the stream) normalized to annual use (load as percent of use, LAPU), the behaviour of atrazine in 414 watersheds across the range of scales was easily compared. It was observed that the LAPU value of atrazine did not vary substantially with scale in watersheds that ranged through 14 orders of magnitude in area. The variability that did exist in the LAPU values was attributed to year-to-year differences in weather within a given watershed and differences in the terrestrial characteristics among the various watersheds. When the logarithm of annual atrazine load was regressed against the logarithm of annual atrazine use, the slope was very close to unity ($1{\cdot}04 \pm 0{\cdot}02$), suggesting that the average runoff behaviour is consistent across a wide range of watershed areas and characteristics. The central tendency of the atrazine LAPU value was defined as the median small-scale LAPU (small scale means agricultural fields and watersheds $<100\,000$ ha). (Only the small watersheds

* Correspondence to: P. D. Capel, US Geological Survey, University of Minnesota, Minneapolis, MN 55455, USA.

Received 1 December 1999
Accepted 15 May 2000

were used to minimize the effect of any in-stream loss of atrazine. Although the losses will be minimal for atrazine, when this method is applied to other pesticides discussed in this paper the losses could be substantial.) The atrazine median small-scale LAPU was 0·66%. On the basis of these observations, Capel and Larson (2000) concluded that the extent of atrazine runoff was determined by the characteristics of atrazine itself (physical/chemical properties, formulation, and application method), as well as terrestrial or climatic factors. This paper will examine 39 pesticides in a similar fashion to determine whether a similar phenomenon is observed.

Many different organic compounds are used to control pests in agricultural crops. Wauchope (1978, p. 450), in his review of the literature on pesticide runoff from agricultural fields, wrote, 'pesticides are different. The only property that these chemicals have in common is their broad function as tools for crop protection. Once they leave the spray nozzle they show vastly different persistences, mobilities, and toxicities'. Each individual organic pesticide has its particular set of physical/chemical properties (solubility, vapour pressure, Henry's law constant, etc.). Each pesticide is generally marketed in only one or a few different formulations (granular, wettable powder, emulsifiable concentrate, etc.) and applied in the field by one or more different methods (surface, soil incorporated, foliar, etc.). These three attributes of a particular pesticide are often interrelated. As an example, butylate, a herbicide used on corn, has a relatively high vapour pressure (Table I) and, consequently, is almost always incorporated into the soil (applied at depth) so that its efficacy will not be lost due to volatilization to the atmosphere.'

Concentrations of 39 current-use pesticides (Table I) have been measured in rivers across the United States in two US Geological Survey (USGS) Programs [National Stream-Quality Accounting Network (NASQAN) and National Water-Quality Assessment Program (NAWQA)]. These data have been used to calculate annual LAPU values. The LAPU values from the USGS programs were combined with LAPU values for studies of the 39 pesticides in runoff and in streams, which are reported in the scientific literature. The LAPUs for individual pesticides from field-scale and watershed-scale studies are examined to help understand the controls on the extent of field runoff and in-stream losses. By comparing the LAPUs for the different chemicals, the relative importance of chemical properties, formulations, and application practices are discussed. On the basis of these observations, a generalized conceptual model of the movement of pesticides from the field to the ocean is suggested.

Factors controlling field runoff

The extent to which a pesticide runs off an agricultural field is determined by the unique combination of climatic, terrestrial, chemical, and management factors that characterize each field, crop, and year combination. Each of these factors has been studied in detail, and numerous reviews on this subject have been published (Wauchope, 1978; Weber *et al.*, 1980; Wauchope and Leonard, 1980; Leonard, 1988, 1990; Willis and McDowell, 1982).

The most important factor controlling the extent of runoff is rainfall, especially the timing and intensity of the first substantial rain after application. The greatest amounts of pesticides are lost from the field when the first runoff-producing rain occurs soon after application. Subsequent runoff-producing rains tend to cause lesser amounts of pesticides to leave the field. Many field runoff studies have used simulated rain to control the timing and amount of the precipitation (Capel *et al.*, 2001). Frequently, investigators exceed normal rainfall amounts in these studies to simulate worse-case conditions. Wauchope (1978) refers to these as catastrophic rain events, and LAPUs >2% are often observed.

Terrestrial factors also influence the extent of pesticide runoff. Important factors that have been identified include soil-particle size and organic-matter content, and topographic slope. Particle size can influence the rate of infiltration of water; generally, smaller particle sizes yield lower infiltration rates and more runoff. Particle size and soil organic-matter content influences runoff by affecting the extent of sorption of the pesticide. Chemicals strongly sorbed to soil particles tend to leave the field associated with particles, whereas chemicals weakly sorbed tend to leave the field in the aqueous phase. Efforts to control soil

Table I. Agricultural pesticide use, properties, and estimated in-stream loss

Pesticide (use[a])	Major application method[b]	National use rank[c]	Soil half-life (days)[d]	Aqueous half-life group[e]	log K_H[f]	log K_{oc}[g]	Major loss process[h]	Estimated % lost in 15 days[i]
Alachlor (H)	sur	7	27	E	−7·67	2·23	T	14
Atrazine (H)	sur	1	173	G	−8·55	2·00	T	2
Azinphos-methyl (I)	fol	48	10	C	−8·51	2·61	T	77
Benfluralin (H)	inc	105	80	C	−3·54	3·95	T,V	95
Butylate (H)	inc	19	28	E	−4·09	2·60	V	74
Carbaryl (I)	fol	32	14	C	−9·36	2·36	T	77
Carbofuran (I)	inc	24	41	C	−9·31	2·02	T	77
Chlorpyrifos (I)	inc	12	43	C	−4·97	3·78	T	86
Cyanazine (H)	sur	3	13	E	−11·53	2·30	T	14
DCPA (H)	sur	76	50	F	−5·57	1·18	T	45
Diazinon (I)	fol	62	7	E	−6·40	2·76	T	16
Disulfoton (I)	fol	60	37	D	−5·67	3·25	T	45
EPTC (H)	inc	13	18	C	−5·00	2·30	T	85
Ethalfluralin (H)	inc	47	41	B	−3·90	3·71	T	100
Ethoprop (I)	inc	67	29	E	−6·85	2·15	T	14
Fonofos (I)	fol	45	37	D	−5·17	2·94	T,V	54
Lindane (I)	sur	161	423	G	−5·84	3·00	V	10
Linuron (H)	sur	54	82	D	−6·13	2·91	T	40
Malathion (I)	fol	40	9	B	−7·65	3·26	T	99
Methyl parathion (I)	fol	16	10	D	−6·69	3·70	T	42
Metolachlor (H)	sur	2	141	E	−7·64	2·26	T	14
Metribuzin (H)	sur	46	47	F	−10·46	1·71	T	36
Molinate (H)	pat	25	13	C	−5·85	1·92	T	79
Napropamide (H)	inc	99	48	C	−9·09	2·66	T	77
Parathion (I)	fol	55	14	D	−6·63	3·88	T	44
Pebulate (H)	inc	90	8	D	−4·59	2·62	T,V	70
Pendimethalin (H)	sur	9	174	F	−4·92	4·13	T,V	67
Permethrin (I)	fol	—	42	D	−5·73	4·59	T,S	66
Phorate (I)	sur	34	37	F	−5·01	2·82	T,V	58
Pronamide (H)	sur	127	45	F	−5·74	2·90	T	43
Propachlor (H)	sur	31	9	D	−6·97	1·90	T	37
Propanil (H)	sur	20	1	A	−7·27	2·17	T	100
Propargite (I)	fol	39	84	F	−7·47	4·61	S,T	65
Simazine (H)	sur	26	89	D	−8·47	2·11	T	36
Terbacil (H)	sur	93	212	G	−9·83	1·74	T	2
Terbufos (I)	inc	21	12	B	−4·62	2·70	T	99
Thiobencarb (H)	pat	64	19	C	−3·54	2·95	T,V	95
Triallate (H)	inc	53	74	E	−4·95	3·38	V	47
Trifluralin (H)	inc	10	81	E	−4·01	4·14	V	79

[a] H: herbicide, I: insecticide.
[b] Sur: soil surface applied; inc: incorporated into soil; fol: foliar applied; pad: added to rice paddy (Wauchope *et al.*, 1992).
[c] Agricultural use rank by mass applied (Gianessi and Anderson, 1996).
[d] USDA, (1999).
[e] A: ~0·5–1 day; B: ~1–4 days; C: ~4–12 days; D: ~12–40 days; E: ~40–120 days; F: ~120–420 days; G: ~420–1200 days; Mackay *et al.* (1997).
[f] log Henry's law constant (K_H, 20 °C, atm m^3 mol^{-1}; USDA, 1999).
[g] log organic-carbon normalized water–solid distribution coefficient (K_{oc}, 1 kg^{-1}; USDA, 1999).
[h] S: sorption/sedimentation; T: transformation; V: volatilization. Two major processes are identified, if they differ by less than a factor of two.
[i] Estimated losses are for the conditions: POC = 1 mg l^{-1}; mean depth, 2 m; mean water velocity, 1 m s^{-1}; temperature, 20 °C; wind speed, 1 m s^{-1}.

erosion could significantly reduce the runoff of strongly sorbed pesticides, but would have little effect on others.

The chemical structure of a pesticide determines its properties. These include water solubility, acid dissociation constant, ionic charge, vapour pressure, and resistance to physically, chemically, and biologically induced transformation reactions. For nonionic compounds, the water solubility is inversely related to the extent of sorption to soil particles. Pesticides with relatively high vapour pressures are easily lost from the soil via volatilization if they are not incorporated into the soil during application. Loss to the atmosphere influences the extent of runoff by diminishing the amount of the pesticide available in the soil. The same holds true for the kinetics of the transformation reactions. The faster any type of reaction transforms the pesticide in the field, the less is available over the season to be lost in runoff.

Wauchope (1978) showed that one way of organizing the runoff behaviour of various pesticides is by their formulations. Pesticides formulated as wettable powders (generally herbicides applied to the soil surface) had the greatest tendency toward runoff of the pesticides still used in agriculture. (The organochlorine insecticides had the greatest tendency to runoff, but most of them are no longer in use.) Wauchope (1978) suggested that a LAPU of about 2% would be a good estimate for compounds formulated as wettable powders for fields with low slopes. Wauchope (1978) also suggested that pesticides formulated as an emulsion had LAPUs of 1% or less. Many of the low solubility compounds and foliar-applied insecticides are in this group. The pesticides that generally had the lowest LAPUs (<0·5%) included the soil-incorporated compounds and the highly water-soluble pesticides that were formulated as aqueous solutions. If only organic pesticides are considered, paraquat was the only consistent exception to these general observations. Although paraquat is highly water soluble, it is cationic and, therefore, strongly associates with soil particles.

Many types of agricultural practice come into play when determining the extent of runoff of pesticides, as well as water and soil, including choice of crop, chemical application method, chemical formulation, tillage method, and best management practices (BMPs). The choices made are based on a consideration of practical, economic, and environmental concerns. The choice of crop and chemical is dependent on climate and soil. The choice of chemical, application method, and tillage method is dependent on the equipment available to the farmer and the application method recommended by the chemical manufacturer. The choice of BMP, such as buffer strips, contour ploughing, or reduced tillage, generally is based on local environmental concerns. Many BMPs are designed to decrease the amount of soil that is lost to surface waters, but a few are designed to reduce water runoff. The different BMPs affect the runoff of the more water-soluble pesticides to various extents.

After a pesticide runs off the field and enters a stream, its behaviour and fate will be governed by the properties of the chemical (particularly water solubility, Henry's law constant, and persistence) and the properties of the stream (particularly travel time, depth, solids concentration, and the physical, chemical, and(or) microbiological constituents that cause transformation). Although the behaviour of each chemical in each river will be unique, there are ranges of chemical and environmental properties that bracket most situations. By examining these ranges, the relative importance of the three general loss processes (transformation, volatilization, and sorption/sedimentation) can be evaluated for individual pesticides in a variety of riverine environments. These model equations, given below, are illustrated with a simple example. The model equations then will be applied to the 39 pesticides included in this study to help understand the field observations.

METHODS

Sampling and analysis

Samples were obtained from the largest rivers (Colorado, Columbia, Mississippi, and Rio Grande Rivers and their major tributaries) in the USA from October 1996 through September 1998 as part of the NASQAN program. For a given pesticide, only those watersheds that met minimum use criteria (1 kg km^{-2}) are included

in this analysis. The number of NASQAN watersheds varies from 0 to 14, depending on the compound. A more detailed description of the watersheds, details of the sampling schedule and the sampling techniques, are described by Hooper *et al.* (2001) and Kelly and Hooper (2001).

Samples were also obtained from 43 streams and rivers from October 1992 through September 1994 as part of the NAWQA program. For a given pesticide, only those watersheds that met minimum use criteria (1 kg km^{-2}) are included in this analysis. The number of NAWQA watersheds varies from 0 to 34, depending on the compound. The smaller watersheds generally were intensively cropped and indicative of the agriculture of the region. A more detailed description of the watersheds, the details of the sampling schedule and the sampling techniques are described by Larson *et al.* (1999) and Shelton (1994).

The NASQAN and NAWQA programs used the same analytical procedure for the pesticides. Briefly, a 1 l water sample was processed through a combusted 142 mm glass-fibre filter (nominal 0·7 μm pore openings). The filtered water was spiked with surrogates. After the pesticides were isolated from the water with a 500 mg octadecyl solid-phase extraction column, the column was dried and the pesticides eluted with solvent. The solvent volume was reduced with a gentle stream of nitrogen. The extract then was analysed by gas chromatography/mass spectrometry using selective ion monitoring. The method detection limits ranged from 1 to 10 ng l^{-1}. Details of the analytical procedure, including quality assurance results, are in Zaugg *et al.* (1995).

Literature data of LAPU values from studies for fields and streams

The international scientific literature was searched for studies that quantified the selected pesticides in field runoff or streams by means of two computerized bibliographic databases: Chemical Abstracts and AGRICOLA. Only articles that contained enough information to calculate a LAPU value were retained. The areas of the controlled field studies ranged from 0·000 023 to 60 ha. The areas of the watershed studies ranged from 58 to 315 620 000 ha. Throughout this paper, both of these groups are referred to as watersheds.

All controlled plot and field studies that were conducted outside of the laboratory and lasted for more than 1 day were included in this analysis without screening. The duration of most field studies was weeks to months. A few, with a shorter duration, employed simulated rain. Because the majority of pesticide runoff almost always occurs in the first major runoff event following application, the results of the short duration studies are similar to the results of the studies of longer duration. The *a priori* decision to include all studies with duration greater than 1 day was made to limit any bias introduced by deleting certain field studies. The exception to this is the single field-scale study that examined EPTC (Spencer and Cliath, 1991). This study examined the loss of EPTC after it was put into irrigation water for alfalfa. Because most EPTC is used on corn and applied as incorporated herbicide, the losses in the irrigation water study would not be representative of the major use of this compound and, therefore, were not included in Table II.

Load calculations and pesticide use estimates

The annual loads of the pesticides in streams from both the NASQAN and NAWQA programs were calculated as described in Larson *et al.* (1995) by summing up estimated daily loads. The daily loads were calculated by multiplying the daily stream discharge by the daily concentration. Daily discharge values were available, but pesticide concentrations were measured less frequently. Pesticide concentrations for days that were not sampled were estimated by linear interpolation from the concentrations measured on the closest preceding and following days in which pesticides were quantified. If the pesticide was not detected, a value of zero was used for the concentration. The loads of the pesticides from studies published in the literature were used as reported. In some cases, loads that were reported as '<' were removed from the statistical analysis described below when the data were transformed by the base-10 logarithm.

For the data from the NASQAN and NAWQA programs, pesticide use was based on county-level use estimates (Gianessi and Anderson, 1996). The estimated use of each pesticide in each county in the watershed was summed to yield a total use value. For counties only partially in the watershed, the pesticide's use was

Table II. Summary of field-based and watershed-based LAPU values of the 39 pesticides. The median small-scale LAPU is based on observations from both field and small watersheds (<100 000 ha)

Compound	Field-based observations (≤60 ha)				Median small-scale LAPU (%)	Stream-based observations (≥100 ha)								
						All		Watersheds < 100 000 ha			Watersheds > 10 000 000 ha			
	N	%<[a]	Median	Mean ± SD		*N*	%<[a]	Median	Mean ± SD	*N*	Median	Mean ± SD	*N*
Alachlor	113	6	0·36	2·1 ± 0·3	0·27	146	5	0·12	0·38 ± 0·83	34	0·13	0·17 ± 0·15	34
Atrazine	181	6	0·76	1·7 ± 0·9	0·66	226	3	0·47	1·7 ± 3·0	95	1·5	1·9 ± 1·5	51
Cyanazine	69	7	0·10	3·7 ± 0·4	0·68	135	5	0·13	1·1 ± 2·5	28	0·82	1·2 ± 1·1	43
DCPA	3	0	1·4	1·3 ± 0·096	1·2	5	0	1·2	1·2 ± 1·1	3	—	—	0
Linuron	16	6	0·040	0·45 ± 0·88	0·038	19	58	0·024	0·090 ± 0·15	10	<	<	6
Metolachlor	102	3	0·60	1·2 ± 0·9	0·50	175	3	0·25	1·0 ± 1·6	54	0·80	1·0 ± 0·82	51
Metribuzin	92	1	0·71	1·8 ± 0·5	0·70	61	8	0·053	0·40 ± 0·73	5	0·28	0·25 ± 0·14	6
Pendimethalin	6	17	0·046	0·035 ± 0·024	0·0050	71	44	0·0043	0·013 ± 0·018	30	<	0·0066 ± 0·0092	24
Pronamide	0	—	—	—	—[b]	1	0	0·020	0·020	1	—	—	0
Propachlor	11	0	0·25	1·4 ± 0·9	0·22	15	27	0·051	0·065 ± 0·053	4	0·0073	0·040 ± 0·068	9
Propanil	0	—	—	—	—[b]	1	0	6·4	—	0	—	—	0
Simazine	26	23	0·16	0·82 ± 0·4	0·52	40	3	1·6	2·6 ± 2·9	12	5·2	6·5 ± 4·7	14
Terbacil	0	—	—	—	—[b]	1	0	0·73	0·73	1	—	—	0
Benfluralin	0	—	—	—	<	4	100	<	<	4	—	—	0
Butylate	0	—	—	—	0·0039	38	44	0·0039	0·082 ± 0·21	13	<	0·019 ± 0·059	15
EPTC[1]	0	—	—	—	0·034	82	12	0·034	0·16 ± 0·47	21	0·0080	0·021 ± 0·037	37
Ethalfluralin	0	—	—	—	<	12	67	<	0·13 ± 0·42	10	—	—	0
Napropamide	0	—	—	—	1·6	3	0	1·6	1·6 ± 0·85	2	—	—	0
Pebulate	0	—	—	—	0·00027	5	40	0·0003	1·0 ± 1·7	3	—	—	0
Triallate	0	—	—	—	0·0023	10	20	0·0022	0·012 ± 0·020	4	<	<	0
Trifluralin	36	11	0·18	0·23 ± 0·25	0·054	69	26	0·012	0·06 ± 0·15	25	0·0043	0·0064 ± 0·0087	24
Molinate	0	—	—	—	4·9	3	0	4·9	4·9 ± 6·7	2	—	—	0

Thiobencarb	0	—	—	—	—	0	—	—	—	0	—	—	0
Azinphos-methyl	7	0	0·52	0·59 ± 0·59	0·32	21	62	0·15	0·42 ± 0·74	6	<	<	6
Carbaryl	1	0	0·14	0·14	0·033	27	37	0·032	0·075 ± 0·086	14	<	<	6
Carbofuran	14	14	0·84	2·3 ± 0·2	0·32	27	30	0·12	0·36 ± 0·70	16	0·090	0·11 ± 0·093	6
Chlorpyrifos	30	20	0·080	0·15 ± 0·20	0·032	71	35	0·0040	0·023 ± 0·035	30	0·0032	0·013 ± 0·030	19
Diazinon	5	20	0·050	0·052 ± 0·037	0·085	19	11	0·085	0·14 ± 0·21	5	0·045	0·22 ± 0·43	6
Disulfoton	0	—	—	—	<	14	86	<	0·0082 ± 0·016	5	<	<	6
Ethoprop	0	—	—	—	0·0080	16	56	0·0080	0·010 ± 0·21	5	<	<	6
Fonofos	18	0	1·6	1·8 ± 0·1	0·80	30	40	0·0041	0·24 ± 0·84	16	0·020	0·032 ± 0·040	6
Lindane	2	0	0·000 45	0·000 45 ± 0·000 21	0·000 45	0	—	—	—	0	—	—	0
Malathion	0	—	—	—	0·045	14	50	0·018	0·18 ± 0·30	3	<	<	6
Methyl parathion	10	0	0·15	0·14 ± 0·13	0·0090	17	82	<	0·0012 ± 0·0030	6	<	<	6
Parathion	6	0	0·33	0·28 ± 0·20	0·19	10	90	<	0·43 ± 0·75	3	<	<	6
Permethrin	8	38	0·014	0·038 ± 0·058	0·0005	1	100	<	<	1	—	—	0
Phorate	0	—	—	—	<	20	100	<	<	11	<	<	6
Propargite	0	—	—	—	<	24	54	<	1·1 ± 2·2	9	<	0·022 ± 0·035	6
Terbufos	18	0	0·60	1·2 ± 0·9	0·000 80	56	93	<	<	20	<	<<	19
$\sum$ Surface herb[c]	619	5	0·60	1·8 ± 0·3	0·49 ($N = 10$)	866	9	0·23	1·1 ± 2·3	278	0·40	1·0 ± 1·6	219
$\sum$ Incorp herb[c]	36	11	0·18	0·23 ± 0·25	0·016 ($N = 6$)	240	29	0·0066	0·16 ± 0·48	88	0·0030	0·014 ± 0·038	82
$\sum$ Insecticides[c]	119	10	0·25	0·84 ± 0·6	0·078 ($N = 14$)	350	57	0·000 58	0·18 ± 0·70	144	<	0·025 ± 0·11	104

[a] Percent less of watersheds in which a LAPU value could not calculated due to water concentrations that were below the detection limit.
[b] Herbicides with median small-scale LAPUs based only on one small watershed observation: pronamide 0·020%, propanil 6·4%, and terbacil 0·73%.
[c] The high and low LAPU values were eliminated and the remaining values averaged.

prorated on the basis of percentage of land used in row crop agriculture in the watershed (Gilliom and Thelin, 1997). For the studies from the literature, the masses of the pesticides applied were used in this analysis as originally reported.

Factors and model equations of in-stream losses of pesticides

Pesticides can undergo physically, chemically, and (or) biologically induced transformation reactions. Depending on the conditions of the environments, different types of transformation process can act simultaneously on a pesticide, but generally one reaction is the most important. The rate of transformation is often described by pseudo first-order kinetics with a rate constant k_t that is the sum of all physically, chemically, and (or) biologically induced reactions. The percent loss as a function of time t can be calculated by

$$(\ln C/C_o) \times 100 = -k_t t \tag{1}$$

where C_o is the initial total concentration and C is the total concentration at time t. Figure 1(a) shows the percent loss of a pesticide as a function of surface water half-life for a range of travel times that bracket most riverine systems. As an example, for a 15 day travel time, typical of the Mississippi River from Iowa to the Gulf of Mexico (Pereira and Rostad, 1990), only those pesticides that have aquatic half-lives less than about 47 days will have losses $\geq$20%.

The rate loss of a pesticide from the water column via volatilization is a function of chemical properties (Henry's law constant and diffusivities in air and water), riverine properties (depth, water temperature and turbulence), and atmospheric properties (air temperature and wind speed). Volatilization is often modelled after the two-film theory, which suggests that the mass flux of the contaminant is the product of the overall mass transfer coefficient v_{OL} and the difference between the concentrations of the pesticide in the water and air. Often expressed as the resistance to air–water transfer, $1/v_{OL}$ is the sum of the resistance of transfer through the two stagnant films (water and air)

$$1/v_{OL} = 1/v_W + 1/v_A \tag{2}$$

where v_W and v_A are the mass transfer coefficients in the stagnant water and air films respectively. Schwarzenbach *et al.* (1993), in their review of the literature, suggest that v_W and v_A can be estimated by the relationships

$$v_W \approx (D_{w,i}/D_{w,O_2})^{0.57}(4 \times 10^{-5}(u_{10})^2 + 4 \times 10^{-4}) \tag{3}$$

and

$$v_A \approx (D_{a,i}/D_{a,H_2O})^{0.67}(0.2u_{10} + 0.3)(K_H/RT) \tag{4}$$

where $D_{w,i}$ (cm^2 s^{-1}), is the diffusivity of compound i in water, D_{w,O_2} (cm^2 s^{-1}) is the diffusivity of oxygen in water, $D_{a,i}$ (cm^2 s^{-1}) is the diffusivity of compound i in air, D_{a,H_2O} (cm^2 s^{-1}) is the diffusivity of water in air, u_{10} (m s^{-1}) is the wind speed at 10 m above the river surface, R (0·082 1 atm mol^{-1} K^{-1}) is the gas constant, T(K) is the temperature, and K_H (l atm mol^{-1}) is Henry's law constant.

Because only the dissolved fraction of the pesticide is available for volatilization, the rate of loss of a pesticide to the atmosphere via volatilization R_v, assuming its air concentration is zero, is

$$R_v = -k_v C(1 - f_p) = -(v_{OL}/z)C(1 - f_p) \tag{5}$$

where k_v is the pseudo first-order rate constant, f_p is the fraction of the pesticide associated with the particulate phase, and z(m) is the mean depth of the river. For a given wind speed, this equation can be rearranged and solved for a specific degree of loss of the pesticide. Assuming a wind speed of 1 m s^{-1}, Figure 1(b) shows the ranges of K_H values and riverine depths that would result in a 20% loss of a pesticide for a range of riverine travel times. Using the example of the Mississippi River described above (z = 2 m), only those pesticides with a K_H value $\geq 1 \times 10^{-3}$ would have a loss of 20% in a 15 day travel time.

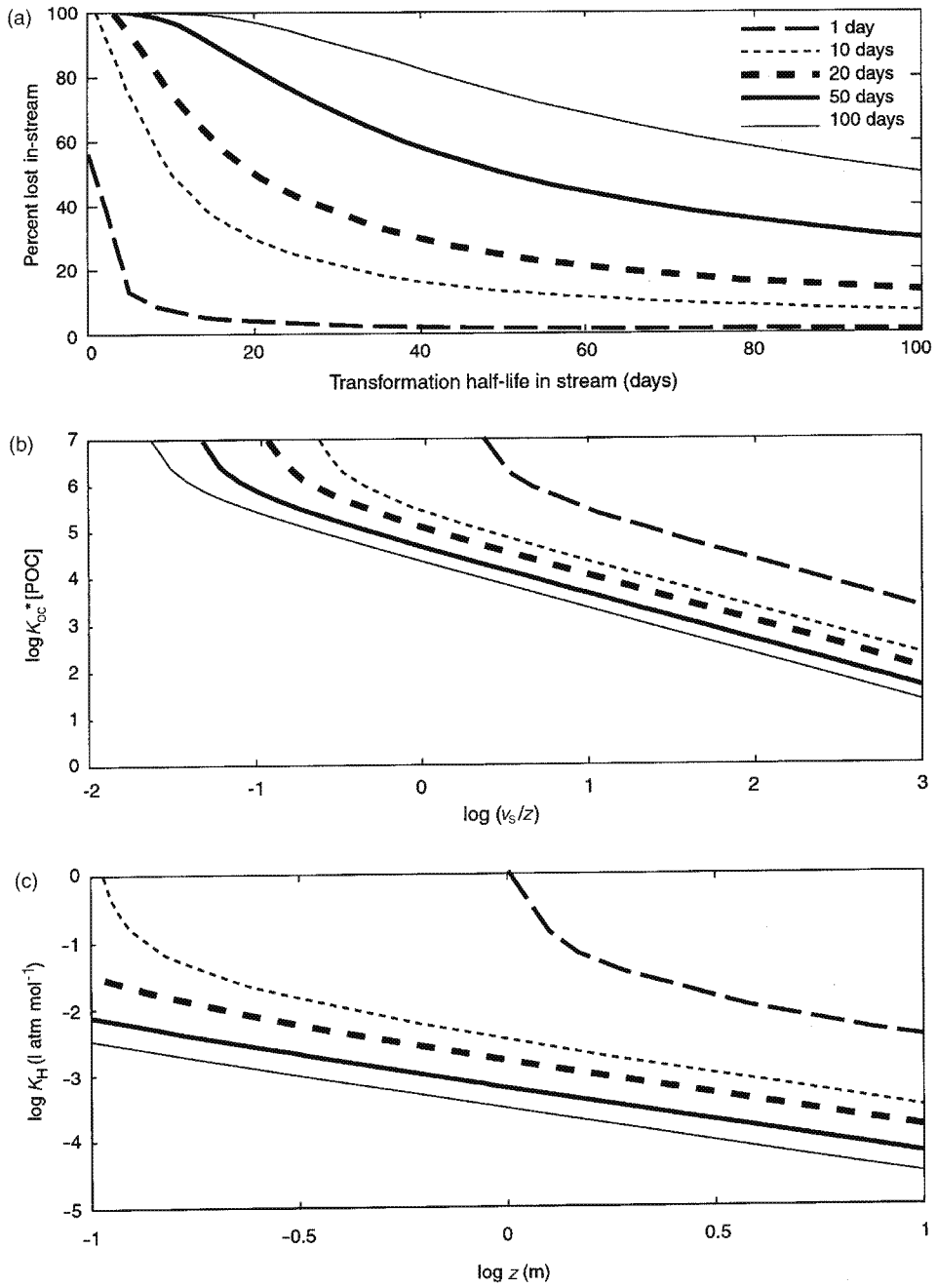

Figure 1. (a) Percent in-stream loss of a pesticide as a function of surface water half-life for a range of travel times that bracket most riverine systems. (b) Typical ranges of Henry's law constant K_H and mean stream depth that would result in a 20% loss of a pesticide for a range of travel times. (Average wind speed assumed to be 1 m s^{-1}.) (c) Typical ranges of the product of organic-carbon based sorption coefficient K_{oc} and particulate organic carbon concentration (POC) and the product of mean stream depth and particle settling velocity that would result in a 20% loss of a pesticide for a range of travel times. In all three graphs, the lines represent a 20% loss for a river similar to the upper Mississippi River and a 15 day travel time

The rate loss of a pesticide from the water column via sorption/sedimentation is conceptually a two-step process. The first step, sorption, is largely governed by the chemical. The physics of the river and the types of aquatic particle largely govern the second step, sedimentation. The driving force for sorption of nonionic pesticides is their hydrophobicity, which is quantified through water solubility. Several investigators (see review in Schwarzenbach *et al.* (1993)) have shown that the extent of sorption for a given chemical is a function of its water solubility and the fraction of the aquatic particle that consists of organic carbon f_{oc}. Wanner *et al.* (1989) have used these relations to calculate the fraction of the chemical in the particulate phase f_p

$$f_p = (K_{oc}[\mathrm{POC}])/(1 + K_{OC}[\mathrm{POC}]) \tag{6}$$

where K_{OC}(l kg^{-1}) organic carbon), is the organic-carbon normalized distribution coefficient and [POC] (kg l^{-1}) is the concentration of particulate organic carbon. This can be rearranged to isolate the effect of the chemical (K_{oc}) and riverine (POC) properties on the fraction in the particulate phase

$$K_{OC}[\mathrm{POC}] = (f_p \times 10^{-6})/(1 - f_p) \tag{7}$$

The factor of 10^{-6} is for unit conversion from 1 kg^{-1} for POC in Equation (6), to the units of mg l^{-1}, the units in which POC is normally reported.

Once the pesticide is sorbed to the particle, it can be removed from the water column through sedimentation. Wanner *et al.* (1989) have suggested that the removal R_s can be described as

$$R_s = -k_s f_p C = -(v_s/z) f_p C \tag{8}$$

where k_s is the pseudo first-order rate constant for sedimentation, v_s is the mean settling velocity, and z is the mean depth of the river. Figure 1(c) shows the range of values of chemical and riverine properties that would result in a 20% loss of a pesticide for a range of riverine travel times. In Figure 1(c), the y-axis brackets the product of the normal ranges of K_{oc} (1 to 10 000 1 kg^{-1}) and [POC] (1 to 100 mg l^{-1}) and the x-axis brackets the product of the normal ranges of v_s (0·01 to 10 m day^{-1}) and z (0·1 to 10 m). As in the example above (v_s = 2 m day^{-1}, z = 2 m, [POC] = 1 mg l^{-1}), only those chemicals with $K_{oc} > 6 \times 10^4$ would have losses of ≥20% in a 15 day travel time.

RESULTS

Plot- and field-scale observations of LAPU

The statistical summary of the LAPUs for the 39 individual compound is presented in Table II. The scales of these plot and field studies ranged from 0·23 m^2 to 60 ha (about six orders of magnitude). For 17 of the 39 compounds, no literature studies were found that reported a LAPU or the data needed to calculate a LAPU. For another eight compounds, fewer than ten LAPUs are reported in the literature. In this group, many of the values reported for a compound were from a single study.

The relationship between the mean and median LAPU values differs among individual compounds. The mean was greater than the median for 16 of the 22 compounds, although the difference between the mean and median LAPU values was less than a factor of two for 14 of the 22 compounds. The largest difference between the mean and median was for cyanazine, which had a very high mean LAPU value because one study used simulated rain and reported ten observations with a LAPU >10% (Baker *et al.*, 1978). There were ten compounds with a mean LAPU >1%, a median LAPU ≥0·6%, or both. This group included seven surface-applied herbicides (alachlor, atrazine, cyanazine, DCPA, metolachlor, metribuzin, and propachlor) and three insecticides (carbofuran, fonofos, and terbufos). Because DCPA has only three observations, it is uncertain whether DCPA belongs in this group of pesticides with high LAPU values.

The surface-applied corn and (or) soybean herbicides (alachlor, atrazine, cyanazine, metolachlor, and metribuzin) were by far the most commonly studied compounds at the plot and field scale (Table II). This group of five compounds accounts for 72% of all of the LAPU values reported for the 39 compounds. Five insecticides had at least ten reported LAPU values, but a LAPU value was reported for only one soil-incorporated herbicide (trifluralin). It should be noted that the three groups have substantially different numbers of observations of LAPU. There were 619, 36, and 119 observations of LAPU for the surface-applied herbicides, soil-incorporated herbicides and insecticides respectively.

All three groups also had some observations of LAPUs that were reported as zero or less than the minimum quantifiable value (Table II). These zero and less-than values represent 5%, 11%, and 10% of the LAPU values for the surface-applied herbicides, soil-incorporated herbicides, and insecticides respectively. The largest observed LAPU values (those >90th percentile) ranged from 5·4 to 23%, 0·47 to 1·1% and 1·9 to 11% for the surface-applied herbicides, soil-incorporated herbicides and insecticides respectively. A t-test done on the LAPU data after transformation using the cubic root obtained a nearly normal distribution. The mean of the LAPUs for the surface-applied group was significantly different from the means of the soil-incorporated and insecticide groups ($p < 0{\cdot}001$ for both).

In his review of pesticides in runoff, Wauchope (1978) made some generalizations based on pesticide formulation and application method. Although some of the studies included in this analysis were also used in Wauchope's work, a considerable amount of additional research was conducted on the runoff characteristics of these chemicals. He suggested that the LAPUs of surface-applied herbicides (triazines and other wettable powders), soil-incorporated herbicides, and insecticides would be about 2%, 0·5%, and 0·5% respectively. This generalization, made over 20 years ago, is in good agreement with the mean LAPU values of the three groups (1·8%, 0·23%, and 0·84% for the surface-applied herbicides, soil-incorporated herbicides and insecticides respectively).

Estimated in-stream losses of specific pesticides

As pesticides run off the field and into the surface water system, they enter an environment that is water dominated rather than particle dominated. The extent of in-stream losses of individual pesticides will vary because of the characteristics of the streams through which they are transported, as well as the characteristics of the chemical itself. The surface water system spans a continuum of streams from agricultural ditches draining a few farm fields up to the large regional rivers that drain into the ocean. Given this diversity, the characteristics of the streams (physical, chemical, and biological) will vary tremendously. It is not possible, in the context of this paper, to model specifically how individual riverine environments will process individual pesticides. Therefore, a 'standard' stream is defined to compare the relative losses of the different pesticides. This stream is defined by the input parameters described above: mean depth, 2 m; mean water velocity, 2 m day^{-1}; mean wind speed, 1 m s^{-1}; temperature (air and water), 20 °C; POC, 1 mg/l^{-1}; neutral pH; a 'typical' microbiological community; and 'typical' spring sunlight conditions. This 'standard' stream is representative of the upper Mississippi River in early June, when the largest load of pesticides is transported.

Because each of the in-stream loss processes is acting on the pesticide simultaneously, the rate constants must be summed to yield an overall rate of loss. On the basis of Equations (1), (5), and (8), the one or two most important loss processes for each chemical for these stream conditions are presented in Table I.

The pesticides in this study were chosen with the criterion that they exist predominately in the dissolved phase in aqueous environments, because only the filtered water was analysed. Because of this, only two pesticides, propargite and permethrin, have sorption/sedimentation as one of their important loss processes. There are some hydrophobic pesticides (i.e. DDT, chlordane) not targeted in this study that would readily be lost from the water column through sorption/sedimentation.

Volatilization is one of their dominant loss processes for ten of the 39 pesticides. Five of these pesticides (benfluralin, pebulate, pendimethalin, triallate, and trifluralin) are herbicides that are generally incorporated in the soil during application because of their volatility. It is interesting to note that other soil-incorporated

herbicides (EPTC, ethalfluralin, and napropamide) were calculated to be lost faster through transformation reactions than through volatilization. Three of the insecticides (fonofos, lindane, and phorate) were calculated to be lost predominately through volatilization. Finally, thiobencarb, a herbicide normally applied to standing water in rice paddies, can be lost through volatilization as well as transformation.

In-stream transformation (chemically and (or) biologically induced reactions) was the predominate loss mechanism for the remainder of the pesticides. The in-stream transformation rates are based on a review of literature data by Mackay *et al.* (1997). The pesticides were classified into seven transformation groups (Table I). The centre of the half-life range for each group was used in these calculations. Although transformation reactions were an important loss mechanism for all of these compounds, the calculated rate of transformation varied greatly among the pesticides. Malathion and propanil were estimated to have half-lives on the order of 1 to 2 days in the stream, whereas others (atrazine, lindane, and terbacil) were estimated to have half-lives on the order of 1 to 3 years.

Stream observations of LAPU

The results of the simple modelling of percent lost in a 15 day travel time (Table I) are in agreement with actual observations of LAPU in the streams. Metolachlor and trifluralin are used as examples of two types of behaviour in Figure 2. Metolachlor is used an example of those compounds that have minimal in-stream loss. Trifluralin is used as an example of those compounds that have substantial in-stream loss. All of the LAPUs for metolachlor and trifluralin, from both field runoff and stream observations, have been combined in Figure 2. There are 278 LAPU values for metolachlor and 105 LAPU values for trifluralin. Although, for a given watershed area, there is substantial variation in the log LAPU values for both metolachlor and trifluralin because of differences in rainfall or irrigation and terrestrial conditions (Capel and Larson, 2000), the overall relations between LAPU and watershed area are different for the two compounds. Metolachlor has the same range of LAPU values throughout the range of scale. On the basis of an ANOVA test, the mean LAPU values

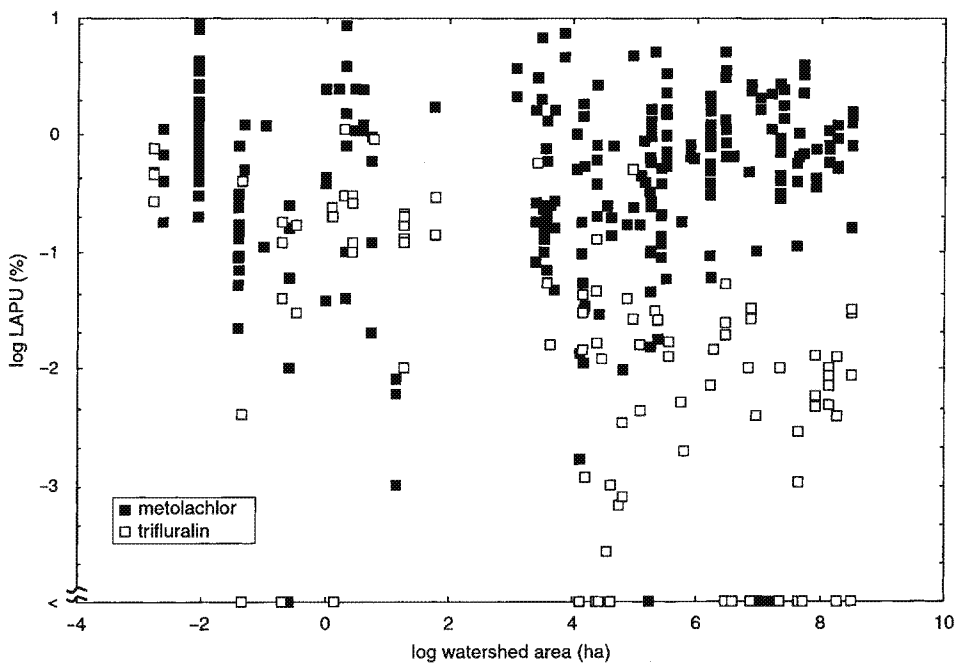

Figure 2. log LAPU (%) as a function of log watershed area (ha) for two herbicides, metolachlor and trifluralin. Data reported for watershed areas < log 2 ha are from field-based studies. Data reported for watershed areas > log 2 ha are from stream-based studies

do not vary among field plots (<60 ha) and small (<10^5 ha), medium (10^5 to 10^7 ha), or large (>10^7 ha) watersheds ($p = 0{\cdot}66$). Also, the slope of the regression line of log LAPU versus log area is essentially zero (0·0033). These two observations suggest strongly that the LAPU values observed in field runoff are in the same range as the LAPU values determined from stream loads and that a minimal amount of metolachlor is lost through in-stream processes. The latter observation is consistent with the prediction reported in Table I. On the other hand, the trend in the LAPU values, as a function of watershed area, is different for trifluralin than for metolachlor. The field-scale (<10^2 ha) observations of log LAPU have little relation with log area, but are statistically different from the LAPUs observed in the streams (Table II, $p < 0{\cdot}001$). The stream observations of LAPU show a trend of decreasing LAPUs with increasing watershed area (Table II). The trend in the observed LAPUs is consistent with the prediction reported in Table I of substantial loss of trifluralin from the stream due to volatilization.

On the basis of the observed LAPUs as a function of watershed area, the behaviour of the 39 pesticides quantified by the NASQAN and NAWQA program fall into three general groups. The first group consists of pesticides that were seldom seen in surface water (Table II). The compounds in this group have low-use amounts (lindane, permethrin, and pronamide, Table I), use only in limited geographical areas (DCPA, ethalfluralin, molinate, pebulate, and thiobencarb), short soil lifetimes (disulfoton, malathion, and parathion), short aquatic lifetimes (propanil and terbufos) and (or) use practices that diminish the chance of runoff, such as soil incorporation (benfluralin, napropamide, and terbufos) or application late in summer when little rain-producing runoff occurs (disulfoton and malathion). Not much information about the behaviour of these compounds can be gleaned from these data, except that their relative absence from the water can be explained, for the most part, on the basis of use, application practice, or relatively fast loss from soil and (or) water. Phorate is the one exception. It was not observed in any of the basins that meet the minimum use criteria, but has relatively high use (ranked 34th nationally in use), is commonly applied at the soil surface, and is estimated to have a relatively low in-stream loss rate (Table I). It is often applied in granular form, so it may not be as available for transport in runoff.

The second group includes those compounds that show little, if any, loss within the stream network. This can be quantified by comparing the LAPU values observed for streams draining smaller watersheds (<10^5 ha) and LAPU values for larger watersheds (>10^7 ha). Because the actual travel times of the pesticides in the streams are unknown, watershed area is used as a surrogate for travel time. Alachlor, atrazine, cyanazine, diazinon, metolachlor, metribuzin, propachlor, and simazine have mean stream LAPU values that differ by less than a factor of two, suggesting that there is relatively little in-stream loss of these compounds. This agrees very well with the results for the simple model predictions, which suggest that these eight compounds have relatively small in-stream losses (<37%) in a 15 day travel time (Table I). Three other compounds, predicted to have this same range of loss from surface water, are not included in this list of eight. These three are ethoprop, lindane, and terbacil. Lindane and terbacil have very low use amounts and are seldom detected in surface waters, so their losses cannot be explained using these data. Ethoprop meets the minimum use criteria in 16 studies, but only seven LAPU values could be calculated, which means that it was also observed infrequently in the streams. This may be due to a combination of relatively low use (ranked 67th in use) and a low potential for transport in runoff (median LAPU value: 0·0080% for watersheds > 100 000 ha). It was observed at low concentrations in the small watersheds, but never quantified in the larger watersheds. This probably is due to dilution, yielding concentrations below the detection limit, rather than in-stream losses, but there is not enough data available to say this conclusively.

The third group consists of those compounds that have a difference in the mean LAPU values greater than a factor of two between the two watershed sizes. In all cases, the LAPU values for the larger watersheds are smaller than the LAPU values for the smaller watersheds. This suggests strongly that there is in-stream loss occurring for these compounds. Because these compounds were observed in the smaller watersheds, the pesticides did move off the fields and into the stream, but a substantial fraction (on average 50 to 100%) was lost during transport in the stream. This group of compounds includes azinphos-methyl, butylate,

carbaryl, carbofuran, EPTC, ethoprop, fonofos, linuron, methyl parathion, pendimethalin, propargite, triallate, and trifluralin.

Another way to divide the selected pesticides is by type and application method: surface-applied herbicides, incorporated herbicides, and insecticides (Table I). On the basis of an ANOVA test, the surface-applied herbicides have significantly greater mean LAPU values in all three categories of watershed area ($<10^5$, 10^5-10^7, and $>10^7$ ha, $p < 0{\cdot}001$ for all three) compared with the incorporated herbicides and insecticides. This is in agreement with the findings from the field runoff studies.

When the LAPU values are compared among the three categories of watershed area, the incorporated herbicides had significantly greater LAPU values in the small watersheds ($<10^5$ ha) than in the largest watersheds ($>10^7$ ha). This is in agreement with loss estimates reported in Table I, where all of the incorporated herbicides had estimated in-stream losses $\geq$70%, except for triallate. In contrast, there is no significant difference in the LAPUs for the surface-applied herbicides among the watershed area categories. This is also consistent with the model predictions. All seven surface-applied herbicides that were frequently observed (alachlor, atrazine, cyanazine, metolachlor, metribuzin, propachlor, and simazine) had estimated in-stream losses $\leq$40%. Finally, there was also no significant difference in the LAPUs for the insecticides, even though the 16 insecticides included in this study have a wide range of estimated in-stream losses (14 to 99%).

Median small-scale LAPU values

The median small-scale LAPU is a measure of the central tendency of the LAPUs of an individual pesticide across a variety of environmental conditions and watershed areas (Table II). The variability around this central tendency is illustrated in Figure 3 for five example herbicides. The median small-scale LAPU is calculated as the median LAPU values for the field studies and the small watershed studies (<100 000 ha). Data from only field and small watershed studies (<100 000 ha) were used to minimize the bias from in-stream losses. A LAPU value of zero was substituted for any '<' in the calculation. Thiobencarb had no measurements of

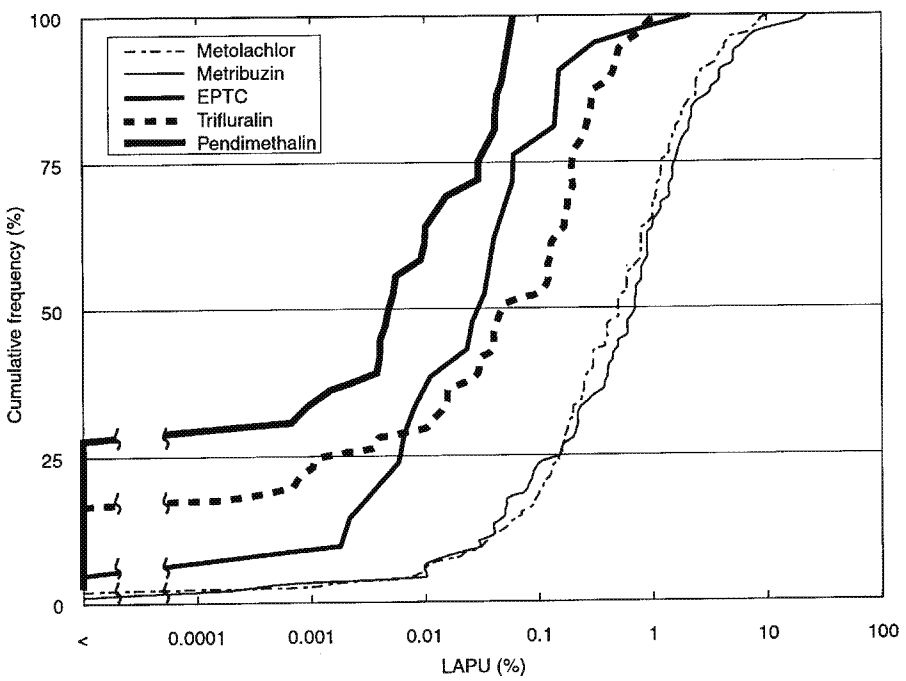

Figure 3. Cumulative frequency diagram of the LAPUs for five herbicides from studies of fields and study plots (<100 ha) and small watersheds (101–100 000 ha)

LAPU in either fields or streams, so no median small-scale LAPU value is reported. Pronamide, propanil, and terbacil had only one watershed observation of LAPU, so was not included in the following discussion.

Three pesticides—DCPA, napropamide, and molinate—had median small-scale LAPU values greater than 1%. Because these three compounds had only a few measured LAPU values, their median small-scale values reported in Table II have a high degree of uncertainty. If the median small-scale LAPUs are ranked for the herbicides, the incorporated herbicides generally have smaller values, and the surface-applied herbicides the larger values. The mean LAPU values for the surface-applied herbicides, incorporated herbicides, and insecticides, are compared in Table II. The median of the median small-scale LAPUs is also much greater for the surface-applied herbicides (0·5%) than the incorporated herbicides (0·0031%). Pendimethalin, a surface-applied corn herbicide, has a much lower median small-scale LAPU compared with the other surface-applied herbicides. It also has a much greater tendency to sorb, as quantified by its log K_{oc} value (Table 1), than the other surface-applied herbicides. Because of the stronger sorption tendencies, the runoff of particles may control the extent of pendimethalin's runoff, whereas the runoff of water may control the extent of runoff of the other more water-soluble surface-applied herbicides.

DISCUSSION

Many factors influence the behaviour of a pesticide from the time of its application to an agricultural field to the time that it is delivered to the ocean. Figure 4 attempts to capture, in a generic manner, the range of behaviour across this range of scale. The axes of Figure 4 are the log of watershed area (to represent scale effects and riverine travel time) *vs* the log of LAPU. This allows both an easy compound-to-compound comparison and a watershed-to-watershed comparison for the same compound, because it normalizes for the amount of use. The vertical line in the figure represents the transition between agricultural field and first-order stream (or drainage ditch). This is the scale at which the pesticide runs off the field and enters the riverine network. The behaviour of five different generic pesticides, denoted A, B, C, D, and E, is plotted, and will be described individually. There are additional details drawn for compound 'A' that are applicable to the other compounds, but not included for the sake of simplicity.

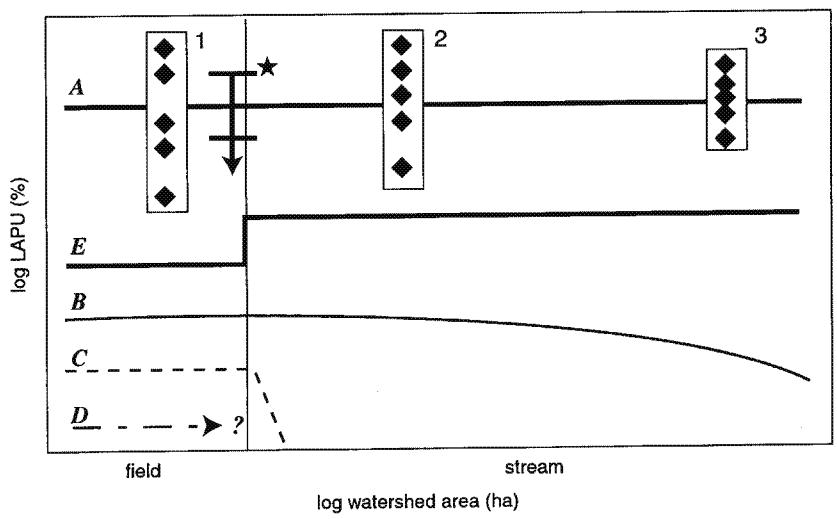

Figure 4. Cartoon of the apparent LAPU value of five generic pesticides (A–E) in their field runoff and surface water transport as a function of scale. Boxes 1–3 represent the year-to-year variability at a given site. The star represents the range of variability in the LAPU for the various terrestrial environments. The median small-scale LAPU for compounds B and C could be anywhere on the *y*-axis. This cartoon just demonstrates their relative in-stream behaviour. Based on field observations, the scale of the *y*-axis (log LAPU in percent) is generally between −4 and 1 (0·0001 and 10%)

The median small-scale LAPU value for a given pesticide is partially controlled by the combination of its application method, formulation, and chemical properties (Capel and Larson, 2000). These three are somewhat interrelated. The variability around the median small-scale LAPU is due to the natural terrestrial environment (soil, slope, etc.) and the standard management practices (tillage, crop, etc.) for that pesticide. In Figure 4, the 'I-beam' at the star represents this variability around the median small-scale LAPU value. Capel and Larson (2000) showed that the median small-scale LAPU value for atrazine was 0·66% and that the central tendency was relatively constant from data collected in watersheds that ranged over 14 orders of magnitude in area. They also showed that part of the variability in the LAPU values for atrazine could be related to the extent of water yield during the period corresponding to the period of maximum atrazine runoff.

The arrow at the bottom of the 'I-beam' (Figure 4 at the star) represents the desired impact of BMPs on pesticide runoff. That is, the implementation of BMPs is supposed to reduce LAPU values. BMPs can be implemented through landscape modifications (i.e. vegetative buffer strips), conservation tillage methods, decreased use of pesticides, and (or) method of application. The first two groups of BMPs, although very important, would most likely decrease the median small-scale LAPU of water-soluble pesticides only slightly. The impact of these types of BMP would probably be measured as part of the inherent variability in the chemical's LAPU value. In Figure 4, this would have the effect of extending the lower portion of the 'I-beam'. On the other hand, decreased use or changes in the application method have the potential for a more significant impact. As an example, if the application method of a herbicide, such as atrazine, is changed from surface-applied to incorporated, its runoff behaviour might be characterized as changing from compound A to compound B in Figure 4.

The numbered boxes represent the year-to-year variability because of weather (or excess irrigation) that can be expected at different points in the range of scale (Capel and Larson, 2000). At the field scale (Figure 4, box 1), the variability is very high because of the influence of individual storms. As observed in many plot studies (Leonard, 1990), it is often the intensity and timing of rainfall with respect to application that determines the extent of runoff of the pesticide for any given year. This year-to-year variability decreases somewhat at the small watershed scale that integrates runoff from tens to hundreds of farm fields (Figure 4, box 2). There will still be years that are 'outliers', compared with the long-term average, caused by drought or very large storms that produce runoff for numerous fields at the wrong time with respect to pesticide application. This was observed with atrazine in the Sugar Creek watershed in Indiana (area: 24 600 ha), where the LAPU values for the 6 years 1993–1998 were 1·3%, 0·80%, 0·82%, 2·2%, 14%, and 2·3% respectively. The year that had a LAPU of 14% had an unexpected storm that came soon after the time of atrazine application (Capel and Larson, 2000). At the largest scale (major rivers, Figure 4, box 3), the year-to-year variability will be less, because of the integration of the runoff from thousands of agricultural fields over a very large area. The timing of application in these large watersheds for any given compound may vary by weeks because of climate differences. There seldom will be weather patterns that would affect the runoff in a large enough area to affect strongly the LAPU observed in the largest rivers.

The differences in the generalized behaviour of each of the representative compounds can be considered. Compound A has a relatively high LAPU value that is constant over the range of scale. This means that a substantial percentage of the amount applied is lost in runoff from the field and that there is little loss within the riverine network. This is the behaviour observed for atrazine, described in detail in Capel and Larson (2000), as well as metolachlor (Figure 2) and alachlor and cyanazine (Table II). The compounds in this group are the pesticides that are most frequently detected and exhibit seasonally elevated concentrations in rivers and streams over the complete range of scale (Larson *et al.*, 1999).

Compound B is representative of a pesticide that has moderate in-stream losses. Because the median small-scale LAPU is determined by the chemical, its formulation, and application method, it can fall anywhere in the range of median small-scale LAPU values. The difference in compound B, compared with compound A, is its accelerated rate of loss in the riverine system. Examples of compound B would be EPTC, trifluralin (Figure 2), and other pesticides in Table II that have losses in the range of 20 to 90% for the example 15 day travel time. These compounds are expected to be seen more frequently and at higher concentrations in small

streams compared with the larger rivers. Because their observed LAPUs will decrease as a function of travel time in the river (Table 2), the extrapolation of stream observations back to field runoff must be done with great caution.

Compound C is similar to compound B, except that its riverine loss processes are much faster. Examples of these compounds include azinphos-methyl, ethalfluralin, malathion, pebulate, and terbufos (Table II). They are seldom detected in surface waters removed from direct agricultural runoff (Larson *et al.*, 1999).

Compound D is representative of those compounds that have very short lifetimes (days) in the soil that are seldom seen in field runoff, such as propachlor and propanil. These compounds are also seldom detected in surface waters (Larson *et al.*, 1999).

Finally, compound E is representative of those compounds that have incorrect (artificially high) LAPU values in watersheds. These pesticides, such as diazinon and simazine, have other substantial uses, in addition to agriculture, that act as sources to the environment. Because the LAPU value defined here is based on agricultural usage (Gianessi and Anderson, 1996), the LAPU value observed in some watersheds will be artificially high. In the USA, diazinon is often observed in surface waters in the Pacific coast states, in the Midwest, and in urban streams (Larson *et al.*, 1999; Hoffman *et al.*, 2000). Diazinon is frequently used in orchards in the West; therefore, some of the soil degradation processes could be by-passed in its transport from tree to stream. Diazinon also has wide-scale home and garden uses in urban areas. Larson *et al.* (1995) have suggested, on the basis of the temporal concentration patterns in the White, Ohio, and Mississippi Rivers, that the dominant source of diazinon to these rivers is urban rather than agricultural.

One goal of agricultural and regulatory managers is to reduce the amount of pesticides that get into, and are transported through, surface waters to minimize the potential impact on the biological community. On the basis of Figure 4, this can be achieved by decreasing the LAPU of current pesticides through BMPs, particularly the application method, or by creating new compounds that are quickly lost in the soil or water and, thus, have small LAPU values. Both of these methods are being used to reduce the load of pesticides in surface waters. Historically, there has been a move to less persistent pesticides (i.e. DDT to organophosphates). There also has been an increase of BMPs to control runoff (i.e. conservation tillage, buffer strips, and contour ploughing). The use of precision agriculture may be used to decrease the amounts of pesticides used on a field and decrease the pesticide load in runoff. Perhaps one of the simplest and most effective BMPs (based on the findings of this study) would be changing the method of application and formulation, when it is possible. There could be a substantial reduction in the amount of herbicides delivered to surface waters if there was a move away from surface application. Of course, such a change must balance considerations of efficacy, crop toxicity, and chemical properties against a decrease in the amount of the herbicide in runoff and the concomitant change in its impact on the health of aquatic ecosystems and humans, and the increased potential for the contamination of ground water.

A pesticide concentration or load in a given stream is the result of the combined processes that affect the extent of runoff and the extent of in-stream losses. To understand properly and characterize its behaviour, both of these sets of processes must be considered together. For atrazine, Capel and Larson (2000) showed that the observations of LAPU in streams across the complete spectrum of scale could be extrapolated back to the extent of field runoff. That is, the LAPU values measured in field runoff were not significantly different from those measured in streams. This same behaviour can be seen for metolachlor in Figure 2. In fact, all of the pesticide included in this study (with sufficient observations to evaluate) had the same range of LAPUs in the smallest streams as in field runoff studies. For many of these compounds, the observed LAPU decreased or went to zero in the larger streams. These observations point to three important components of pesticide behaviour that must be considered when interpreting monitoring data and making regulatory decisions. First, the results of field runoff studies are directly applicable to estimating the amounts of pesticides delivered to surface water systems. Second, many pesticides are lost within the surface water system, some quite quickly. Therefore, infrequent detection of individual pesticides in streams does not necessarily mean that they were not initially delivered from the field to the stream. Third, each pesticide is a different organic chemical and,

thus, will behave uniquely with respect to its environmental transport, fate, and effect on human and ecosystem health.

The concern over the occurrence of pesticides in surface waters is largely driven by their potential impacts on human and ecosystem health. In many ways, the concerns change as a function of stream size. In smaller streams, the focus of concern is on ecosystem health. Smaller streams make up the majority of riverine miles and provide important habitat for reproduction of aquatic organisms. There are relatively few public drinking water intakes on very small streams. The concern in larger streams and rivers focuses more on human health because they more commonly serve as sources of drinking water. The larger streams also tend to have numerous perturbations (industrial chemical inputs, thermal inputs, dredging, etc.) that have permanently changed the natural ecosystem. Although the impact of pesticides in large rivers may still be important, it is only one of many potential impacts on their ecosystems. (The exceptions to this are the persistent, organochlorine insecticides that readily bioaccumulate. They are of concern to both human and ecosystem health throughout the entire spectrum of watershed areas.) Given these changing concerns with stream size, it should be reiterated that each pesticide is a different organic chemical and, thus, will behave uniquely in its environmental transport, fate, and effect on human and ecosystem health. Only through detailed runoff studies and broad-scale stream monitoring, in conjunction with insights provided by process-based models, can the behaviour of individual pesticides be characterized to the extent that is needed to interpret monitoring results fully and make regulatory decisions.

ACKNOWLEDGEMENTS

This work was supported by USGS NASQAN and NAWQA programs. The use of trade names in this paper is for identification purposes only and does not imply endorsement by the USGS.

REFERENCES

Baker JL, Laflen JM, Johnson HP. 1978. Effect of tillage systems on runoff losses of pesticides, a rainfall simulation study. *Transactions of the American Society of Agricultural Engineers* **21**: 886–892.

Capel PD, Larson SJ. 2000. Effect of scale on the behaviour of pesticides in surface waters: atrazine as an "ideal" example. *Environmental Science and Technology* **35**: 648–657.

Capel PD, Larson SJ, Winterstein TA. 2001. Summary of selected data from field studies of pesticide runoff to surface waters. *US Geological Survey, Water-resources investigations report*. 00-4284; 114.

Gianessi LP, Anderson JE. 1996. *Pesticide Use in U.S. Crop Production*. National Center for Food and Agricultural Policy: Washington, DC.

Gilliom RJ, Thelin GP. 1997. Classification and mapping of agricultural land for the National Water-Quality Assessment program. *US Geological Survey Circular 1131*; 70.

Hoffman R, Larson SJ, Capel PD. 2000. Comparison of pesticides in eight urban streams. *Environmental Toxicology and Chemistry* **19**: 2249–2258.

Hooper RP, Aulenbach BT, Kelly VJ. 2001. The National Stream Quality Accounting Network: a flux-based approach to monitoring the water quality of large rivers. *Hydrologic Processes*: this issue.

Kelly VJ, Hooper RP. 2001. NASQAN—The USGS National Stream-Quality Accounting Network. URL http://water.usgs.gov/nasqan Accessed 23 February 2001.

Larson SJ, Capel PD, Goolsby DA, Zaugg SD, Sandstrom MW. 1995. Relations between pesticide use and riverine flux in the Mississippi River basin. *Chemosphere* **31**(5): 3305–3321.

Larson SJ, Gilliom RJ, Capel PD. 1999. Pesticides in steams of the United States—initial results for the National Water-Quality Assessment program. *US Geological Survey. Water-Resources Investigations Report No. 98–4222*; 92.

Leonard RA. 1988. Herbicides in surface waters. In *Environmental Chemistry of Herbicides*, Grover R (ed.). CRC Publishing Company: Boca Raton, FL; 45–81.

Leonard RA. 1990. Movement of pesticides into surface waters. In *Pesticides in the Soil Environment*, Cheng HH (ed.). Soil Science Society of America: Madison, WI; 303–349.

Mackay D, Shiu WY, Ma KC. 1997. *Illustrated Handbook of Physical–Chemical Properties and Environmental Fate for Organic Chemicals*, Vol. V, *Pesticide Chemicals*. Lewis Publishers: New York; 812.

Pereira WE, Rostad CE. 1990. Occurrence, distributions, and transport of herbicides and their degradation products in the lower Mississippi River and its tributaries. *Environmental Science and Technology* **24**: 1400–1406.

Schwarzenbach RP, Gschwend PM, Imboden DM. 1993. *Environmental Organic Chemistry*. Wiley and Sons, Inc.: New York; 681.

Shelton LR. 1994. Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment Program. *US Geological Survey Open-File Report No. 94–455*; 42 pp.

Spencer WF, Cliath MM. 1991. Pesticide losses in surface runoff from irrigated fields. *Environmental Science Research* **42**: 277–289.

USDA. 1999. Pesticide property database, http://wizard.arsusda.gov/rsml/ppdb.html. Accessed on 15 March, 2000.

Wanner O, Egil T, Fleischmann T, Lanz K, Reichert P. 1989. Behavior of the insecticides disulfoton and thiometon in the Rhine River: a chemodynamic study. *Environmental Science and Technology* **23**: 1232–1242.

Wauchope RD. 1978. The pesticide content of surface water drainage from agricultural fields. *Journal of Environmental Quality* **7**: 459–472.

Wauchope RD, Leonard RA. 1980. Maximum pesticide concentrations in agricultural runoff: a semiempirical prediction formula. *Journal of Environmental Quality* **9**(4): 665–672.

Wauchope RD, Buttler TM, Hornsby AG, Augustijn-Beckers PWM, Burt JP. 1992. The SCS/CES pesticide properties database for environmental decision-making. *Reviews of Environmental Contamination and Toxicology* **123**(1): 1–164.

Weber JB, Shea PJ, Strek HJ. 1980. An evaluation of nonpoint sources of pesticide pollution in runoff. In *Environmental Impact of Nonpoint Source Pollution*, Overcash MR, Davidson JM (eds). Ann Arbor Press: Ann Arbor, MI; 69–98.

Willis GH, McDowell LL. 1982. Pesticide in agricultural runoff and their effects on downstream water quality. *Environmental Toxicology and Chemistry* **1**(1): 267–279.

Zaugg SD, Sandstrom MW, Smith SG, Fehlberg KM. 1995. Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring. *US Geological Survey Open-File Report 95–181*; 49 pp.